

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C03C 13/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/43923</b> <b>(43) International Publication Date:</b> 8 October 1998 (08.10.98)
<b>(21) International Application Number:</b> PCT/US98/05636 <b>(22) International Filing Date:</b> 20 March 1998 (20.03.98)  <b>(30) Priority Data:</b> 08/827,571 28 March 1997 (28.03.97) US  <b>(71) Applicant:</b> JOHNS MANVILLE INTERNATIONAL, INC. [US/US]; 717 Seventeenth Street, Denver, CO 80202 (US).  <b>(72) Inventors:</b> HARDING, Foster, Laverne; 7936 Glen Ridge Drive, Castle Rock, CO 80104 (US). BAUER, Jon, Frederick; 8410 North Pinewood Drive, Castle Rock, CO 80104 (US). RUSSELL, Harry, Hand, III; 17688 Whirlaway Trail, Evergreen, CO 80439 (US). XU, Xiaojie; 11164 West Fremont Place, Littleton, CO 80127 (US).  <b>(74) Agent:</b> TOUSLEE, Robert, D.; Johns Manville Corporation, 10100 West Ute Avenue, Littleton, CO 80127 (US).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> BIOSOLUBLE POT AND MARBLE (FLAME ATTENUATED)-DERIVED FIBERGLASS  <b>(57) Abstract</b>  Glass compositions suitable for pot and marble fiberization display excellent chemical resistance to both acids and moisture while being highly biosoluble at the same time. The glass compositions are characterized by ratios of components which are reflective of acid resistance, biosolubility, and moisture resistance. Preferred glasses have a difference between HTV (10 <sup>3</sup> poise) and liquidus greater than 500 °F, and a biodissolution greater than about 350 ng/cm <sup>2</sup> /hr.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## BIOSOLUBLE POT AND MARBLE (FLAME ATTENUATED)-DERIVED FIBERGLASS

**Technical Field**

5       The present invention pertains to fiberglass products prepared from glass compositions suitable for fiberization by the pot and marble process. The glass fibers exhibit enhanced biosolubility while maintaining other desirable properties.

**Description of the Related Art**

10       Fiberglass has a myriad of uses, including the reinforcement of polymer matrix composites; preparation of thermoformable intermediate products for use as headliners and hoodliners in vehicles; air and water filtration media; and sound and thermal insulation  
15       products. The preparation and/or subsequent processing of such materials often involves handling steps which result in cut or broken fibers which may be inhaled. As it is impractical or impossible to remove such fibers from the body, it has become important to create glass  
20       compositions which exhibit high degrees of biosolubility, i.e. which are rapidly solubilized in biological fluids.

      If high biosolubility were the only factor which need be considered, a solution to the biosolubility problem would be rapidly attained. However, in  
25       addition to being biosoluble, glass fibers must also possess a number of other physical and chemical characteristics. For example, in many applications such as in battery separators, high chemical (e.g. acid) resistance  
30       is required. As can be readily imagined, high chemical

resistance and high biosolubility are largely conflicting characteristics.

5 Glass fibers must also be strong and moisture-resistant. If moisture weakens glass fibers appreciably, their applicability to many uses suffers. Weakened glass fibers not only possess less than desired tensile strength and modulus, but also break and fracture more easily, thus increasing the risk of inhalation, etc. By the same token, moisture resistant glass fibers which  
10 have low strength to begin with also do not fulfill many requirements. For example, building insulation is shipped in compressed form. If the glass fibers of the insulation product are weak or brittle, many fibers will be broken during compression, not only increasing the  
15 number of small fibers which are bioavailable, but also producing an inferior product which may not recover a sufficient amount of its pre-compressed thickness. Strong fibers which are not moisture resistant also exhibit a great deal of breakage, especially under humid  
20 storage, as illustrated hereinafter. Finally, glass fibers must be prepared from glass compositions which can be economically processed.

The two principle methods of glass wool fiber production are the pot and marble process and the  
25 centrifugal or "rotary" process. In the latter, molten glass enters a centrifugal spinner from the forehearth of a glass melting furnace. As the centrifugal spinner rotates, relatively large diameter glass strands stream from orifices located in the spinner's periphery. These  
30 large diameter strands immediately contact an intense hot gas jet produced by burners located around the spinner. The hot gas attenuates the large diameter

strands into fine, elongated fibers, which may be collected on a moving belt.

As glass is an amorphous rather than crystalline "solid", crystallization in the melt or during fiberization will disrupt the fiber glass forming process with disastrous results. In the rotary process, the glass ingredients are first melted in a glass melter prior to their entry into the forehearth. Thus, the feed to the forehearth is high temperature, molten glass. From the forehearth, the molten glass fed to the spinner is cooled to the HTV (high temperature viscosity) or "fiberization" temperature. Because the forehearth is fed with hot, molten glass, and the temperature of the glass in the forehearth is above the HTV, the difference in temperature between the HTV and liquidus (" $\Delta T$ "), the temperature which defines the boundary of crystallization, may be quite small in the rotary process.

In the pot and marble process, relatively large diameter "primary" strands of glass (primaries) exude from holes located in the bottom of the pot. Because room temperature marbles are continuously or incrementally added to the pot, numerous locations will exist within the pot where the temperature might fall below the liquidus temperature, thermodynamically favoring crystallization and disrupting the process. To ensure that the process is not disrupted, glass compositions must be used which exhibit a significant difference, minimally 300°F, between the HTV and liquidus temperatures. Thus, glass compositions formulated for the rotary process, having low  $\Delta T$ , are not suitable for use in pot and marble process.

The primary s exiting the pot from the pot and marble process are flame attenuated rather than hot gas attenuated, thus exposing the glass fibers to higher temperatures than in the rotary process. These higher temperatures cause a loss of the more volatile compounds of the glass composition from the outside of the fibers, resulting in a "shell" which has a different composition than the fiber interior. As a result, the biosolubility of glass fibers prepared from pot and marble fiberglass is not the same as that derived from the rotary process. As glass fibers must necessarily dissolve from the fiber ends or the cylindrical exterior, a more highly resistant shell will drastically impede the biodissolution rate.

15

### Summary Of The Invention

It has now been surprisingly discovered that glass fibers of enhanced biosolubility may be prepared from glass compositions suitable for pot and marble processing, which exhibit minimally about a 350°F difference in HTV and liquidus, and which have well defined formulations meeting both narrow mol percentage composition as well as meeting each of three specific "C-ratios" which govern chemical resistance, moisture resistance, and biosolubility.

25

### Description of the Preferred Embodiments

The subject invention glasses have HTV and liquidus which are suitable for production of glass fibers in the pot and marble process. Such glass generally must have an HTV ( $10^3$  poise) of 1800°F to



2100°F, preferably 1900°F to 2000°F, and exhibit a liquidus which is minimally about 350°F, preferably 425°F, and more preferably 500°F or more lower than the HTV. These characteristics are necessary to prepare  
 5 glass fibers economically on a continuous basis.

The glass composition must fall within the following range of composition, in mol percent:

	SiO <sub>2</sub>	66 -- 69.7
	Al <sub>2</sub> O <sub>3</sub>	0 -- 2.2
10	RO	7 -- 18
	R <sub>2</sub> O	9 -- 20
	B <sub>2</sub> O <sub>3</sub>	0 -- 7.1

where R<sub>2</sub>O is an alkali metal oxide and RO is an alkaline earth metal oxide. R<sub>2</sub>O is preferably Na<sub>2</sub>O in most  
 15 substantial part, while RO may be MgO and/or CaO, preferably both, in a molar ratio of MgO/CaO of 1:3 to 3:1, more preferably 2:3 to 3:2. The chemical behavior of the glass is dictated by three ratios which the glass composition must meet, C(acid), C(bio), and C(moist).  
 20 These ratios are defined compositionally as follows, all amounts being in mol percent:

$$C(\text{acid}) = [\text{SiO}_2] / ([\text{Al}_2\text{O}_3] + [\text{B}_2\text{O}_3] + [\text{R}_2\text{O}] + [\text{RO}])$$

$$C(\text{bio}) = ([\text{SiO}_2] + [\text{Al}_2\text{O}_3]) / ([\text{B}_2\text{O}_3] + [\text{R}_2\text{O}] + [\text{RO}])$$

$$C(\text{moist}) = ([\text{SiO}_2] + [\text{Al}_2\text{O}_3] + [\text{B}_2\text{O}_3]) / ([\text{R}_2\text{O}] + [\text{RO}]).$$

25 In these ratios, C(acid) is the ratio which pertains to chemical resistance in acid environments, C(bio) is the ratio which is most closely linked to biosolubility, and C(moist) is the ratio which relates to retention of properties in moist environments. It is desired that  
 30 C(acid) and C(moist) be as large as possible, while C(bio) should be as low as possible. At the same time,

the HTV and liquidus of the overall composition must be suitable for glass fiber processing. It has been found that pot and marble glass of high biosolubility, while yet maintaining other necessary physical properties such as chemical resistance and moisture resistance, is obtained when  $C(\text{acid}) \geq 1.95$ ,  $C(\text{bio}) \leq 2.30$ , and  $C(\text{moist}) \geq 2.40$ .

Preferably, the biosoluble fiberglass of the subject invention has a composition which falls within the following ranges (in mol percent):

	$\text{SiO}_2$	66 -- 69.0
	$\text{Al}_2\text{O}_3$	0 -- 2.2
	RO	7 -- 16
	$\text{R}_2\text{O}$	9 -- 19
15	$\text{B}_2\text{O}_3$	0 -- 7.1

Most preferably, the biosoluble glass fibers of the subject invention have a composition which falls within the following most preferred range:

	$\text{SiO}_2$	66 -- 68.25
20	$\text{Al}_2\text{O}_3$	0 -- 2.2
	RO	7 -- 13
	$\text{R}_2\text{O}$	11 -- 18
	$\text{B}_2\text{O}_3$	0 -- 7.1

With respect to the performance characteristics of the glass fibers of the subject invention, it is preferred that  $C(\text{acid})$  be greater than or equal to 2.00;  $C(\text{bio})$  be less than or equal to 2.23, more preferably less than or equal to 2.20; and that  $C(\text{moist})$  be greater than or equal to 2.50, preferably greater than or equal to 2.60. As discussed previously, it is most desirable that  $C(\text{acid})$  and  $C(\text{moist})$  be as high as possible. For example,  $C(\text{moist})$  values of 3.00 or greater are particularly preferred. It should be noted also, that the

various C-ratios are independent in the sense that a more preferred glass need not have all "more preferred" C-ratios.

5           Acid resistance may be measured by battery  
industry standard tests. For example, a typical test  
involves addition of 5 grams of nominally 3  $\mu\text{m}$  diameter  
fiber in 50 mL of sulfuric acid having a specific  
gravity of 1.26. Following refluxing for 3 hours, the  
acid phase may be separated by filtration and analyzed  
10 for dissolved metals or other elements.

          The procedure used to evaluate biodissolution  
rate is similar to that described in Law et al. (1990).  
The procedure consists essentially of leaching a 0.5  
gram aliquant of the candidate fibers in a synthetic  
15 physiological fluid, known as Gamble's fluid, or syn-  
thetic extracellular fluid (SEF) at a temperature of  
37°C and a rate adjusted to achieve a ratio of flow rate  
to fiber surface area of 0.02 cm/hr to 0.04 cm/hr for a  
period of up to 1,000 hours duration. Fibers are held  
20 in a thin layer between 0.2  $\mu\text{m}$  polycarbonate filter  
media backed by plastic support mesh and the entire  
assembly placed within a polycarbonate sample cell  
through which the fluid may be percolated. Fluid pH is  
regulated to 7.4 + 0.1 through the use of positive  
25 pressure of 5%  $\text{CO}_2$ /95%  $\text{N}_2$  throughout the flow system.

          Elemental analysis using inductively coupled  
plasma spectroscopy (ICP) of fluid samples taken at  
specific time intervals are used to calculate the total  
mass of glass dissolved. From this data, an overall  
30 rate constant could be calculated for each fiber type  
from the relation:

$$k = [d_0(1-(M/M_0)^{0.5})]/2t$$

where k is the dissolution rate constant in SEF,  $d_0$  the initial fiber diameter,  $\rho$  the initial density of the glass comprising the fiber,  $M_0$  the initial mass of the fibers, M the final mass of the fibers ( $M/M_0$  = the mass fraction remaining), and t the time over which the data was taken. Details of the derivation of this relation is given in Leineweber (1982) and Potter and Mattson (1991). Values for k may be reported in ng/cm<sup>2</sup>/hr and preferably exceed a value of 150. Replicate runs on several fibers in a given sample set show that k values are consistent to within 3 percent for a given composition.

Data obtained from this evaluation can be effectively correlated within the sample set chosen - dissolution data used to derive k's were obtained only from experimental samples of uniform (3.0  $\mu$ m) diameter and under identical conditions of initial sample surface area per volume of fluid per unit time, and sample permeability. Data was obtained from runs of up to 30 days to obtain an accurate representation of the long term dissolution of the fibers. Preferred biodissolution rate constants in ng/cm<sup>2</sup>/hr are greater than 150 ng/cm<sup>2</sup>/hr, preferably greater than 200 ng/cm<sup>2</sup>/hr, more preferably greater than 300 ng/cm<sup>2</sup>/hr, and most preferably greater than 400 ng/cm<sup>2</sup>/hr.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

## Examples

### Comparative C1 and C2

C-ratios are calculated for a conventional C-glass (chemically resistant glass) and a "soluble" glass as disclosed in Examples 1a and 2b in Table 1 of U.S. Patent No. 5,055,428. The glass composition is in weight percent. HTV ( $10^3$  poise) and liquidus are as reported in the '428 patent.

**TABLE 1**

		Comparative Example 1 (Wt%)	Comparative Example 2 (Wt%)
10	SiO <sub>2</sub>	66.4	66.7
	Al <sub>2</sub> O <sub>3</sub>	1.2	1.0
	B <sub>2</sub> O <sub>3</sub>	11.0	10.0
	Na <sub>2</sub> O	12.9	13.9
	K <sub>2</sub> O	0.2	0.2
15	CaO	4.8	5.5
	MgO	3.2	2.5
	C(acid)	2.03	2.07
	C(bio)	2.09	2.13
	C(moist)	3.41	3.29
20	HTV (10 <sup>3</sup> poise)	1965°F	1949°F
	Liquidus	1738°F	1702°F

As can be seen from Table 1, the C-ratios of these rotary process glasses indicate that they should

both have good performance with respect to acid resistance, moisture resistance, and biosolubility. The Comparative Example 2 glass is reported by the patentee to have a dissolution rate in model physiological saline (composition not disclosed) of 211 ng/cm<sup>2</sup>/hr. However, examination of the HTV and liquidus temperatures reveals that these differ only by 227°F and 247°F, respectively. Thus, these glass compositions cannot be used in pot and marble fiberization. These Comparative Examples serve to illustrate the ease with which higher biosolubility can be obtained in rotary processable glass. These glasses cannot be used to manufacture fiberglass by the pot and marble process. However, even were this possible, the flame attenuation and consequent loss of volatile oxides from the fiber surface would be expected to lower the measured biodissolution rate by a factor of from about 2 to 4.

### Examples 1 and 2

Two glass formulations were processed into marbles for use in pot and marble fiberization, and glass fibers prepared in the conventional manner. The formulations, C-ratios, HTV (10<sup>3</sup> poise), liquidus, and measured biosolubility are presented in Table 2. The ingredients are in mol percent.

**TABLE 2**

	Example 1 (mol %)	Example 2 (mol %)
SiO <sub>2</sub>	67.24	67.18
Al <sub>2</sub> O <sub>3</sub>	1.04	1.02
B <sub>2</sub> O <sub>3</sub>	6.08	5.99
CaO	4.99	4.87
MgO	5.24	5.26
Na <sub>2</sub> O	15.22	15.45
K <sub>2</sub> O	0.26	0.23
C(acid)	2.05	2.05
C(bio)	2.15	2.14
C(moist)	2.89	2.87
Biosol K(dis)	350	426
HTV	1972	1981
Liquidus	1435	< 1325

The C-ratios indicate that the glasses of Table 2 should exhibit desirable chemical resistance (both acid and moisture) as well as high biodissolution. The high biodissolution is confirmed by actual tests, being in both cases, considerably greater than 300 ng/cm<sup>2</sup>/hr.

**Example 3. Comparative Examples C3 and C4**

A subject invention glass is compared with two commercial glasses for acid resistance and moisture

resistance, respectively. The formulations (mol per-cent) are as follows.

**TABLE 3**

	Example 3	Example C3	Example C4
SiO <sub>2</sub>	67.28	65.36	57.53
Al <sub>2</sub> O <sub>3</sub>	1.04	1.83	3.11
B <sub>2</sub> O <sub>3</sub>	6.00	4.59	7.23
CaO	4.00	6.27	8.82
Na <sub>2</sub> O	15.20	15.56	16.24
K <sub>2</sub> O	0.26	0.45	0.71
F <sub>2</sub>	--	1.43	--
C(acid)	2.06	1.96	1.35
C(bio)	2.16	2.14	1.54
C(moist)	2.89	2.67	2.11
MgO	5.23	4.52	6.36

The acid resistance of the Example 3 glass was compared with that of Comparative Example C3. It is noted that the Comparative Example C3 glass meets the C-ratio requirements but not the compositional limitations. The results of the acid resistance test are presented below in Table 3a.



**TABLE 3a**

Glass	Example 3	Example C3
Element	Quantity Dissolved (ppm)	Quantity Dissolved (ppm)
Al	187	453
Ca	2831	4110
Mg	854	938

5

10

15

To determine moisture resistance, a stress corrosion test is used in which the fibers are stressed by bending in a controlled humidity and temperature test chamber. Fibers which exhibit moisture resistance under these conditions take longer to break. The Example 3 glass was compared to Comparative Example C4 glass, a glass used commercially for building insulation where compression of insulation and storage generates the potential for fiber breakage as a result. After 50 hours, only 12% of the Example 3 glass had broken, while all of the Comparative Example C4 fibers had failed.

**Comparative Examples C5 and C6**

20

C-ratios are calculated for the rotary process glasses of Example 3 of U.S. Patent No. 4,510,252, and Example 2 of U.S. Patent No. 4,628,038. Composition, calculated C-ratios, liquidus, and estimated HTV ( $10^3$  poise) are given below in Table 4, in mol percent.

**TABLE 4**

	Example C5	Example C6
SiO <sub>2</sub>	68.2	66.67
Al <sub>2</sub> O <sub>3</sub>	2.2	2.25
B <sub>2</sub> O <sub>3</sub>	5.0	4.78
Na <sub>2</sub> O	9.2	8.68
K <sub>2</sub> O	--	0.26
CaO	11.9	14.77
MgO	3.5	3.60
C(acid)	1.85	1.94
C(bio)	2.03	2.15
C(moist)	2.54	2.70
HTV (10 <sup>3</sup> poise), est.	2280°F	2210°F
Liquidus	1983°F	2035°F

As can be seen from the table, the acid resistance of Comparative Example C5 is expected to be low, and the biodissolution is expected also to be low, although the glass should display good moisture resistance. However, the difference between HTV (10<sup>3</sup> poise) and liquidus is only about 297°F, and thus this glass is not suitable for use in a pot and marble process. The glass of Comparative Example C6 exhibits C(acid) close to an acceptable value, although C(bio) is too high. The glass should have good moisture resistance. However, the glass cannot be used in a pot and marble process

as the difference between liquidus and HTV ( $10^3$  poise) is only 175°F.

Comparative Example 7

C-ratios and composition data (mol percent)  
5 are presented for Example 6 of U.S. Patent No. 5,108,957.

**TABLE 5**

	Example C7
SiO <sub>2</sub>	69.55
Al <sub>2</sub> O <sub>3</sub>	0.08
CaO	7.46
MgO	4.30
Na <sub>2</sub> O	15.05
K <sub>2</sub> O	0.04
B <sub>2</sub> O <sub>3</sub>	3.52
C(acid)	2.28
C(bio)	2.29
C(moist)	2.72
HTV ( $10^3$ poise)	2003°F
Liquidus	1706°F

The biodissolution for this glass should be marginal, however the moisture and acid resistance should be acceptable. However, the difference in HTV

and liquidus ( $\Delta T$ ) indicates that this glass is unsuitable for pot and marble fiberization.

**Examples 4-12**

5 Additional glass compositions which fall within the subject invention parameters are presented in the following table.

EXAMPLES 4-12

	Example 4 Mol %	Example 5 Mol %	Example 6 Mol %	Example 7 Mol %	Example 8 Mol %	Example 9 Mol %	Example 10 Mol %	Example 11 Mol %	Example 12 Mol %
SiO <sub>2</sub>	67.28	67.4	66.38	66.9	65.96	68.03	69.08	67.96	68.61
Al <sub>2</sub> O <sub>3</sub>	1.04	1.03	2.35	2.37	2.33	0	0	0	0
B <sub>2</sub> O <sub>3</sub>	6.00	6.06	3.49	7.03	6.93	0.75	3.42	3.37	6.8
Na <sub>2</sub> O	15.20	15.25	17.13	16.08	9.25	16.08	17.58	11.63	9.83
K <sub>2</sub> O	0.26	0.19	0.52	0	0.51	0	0	0	0
CaO	4.99	4.83	4.87	3.76	7.42	7.43	4.89	8.46	7.28
MgO	5.23	5.23	5.27	3.87	7.63	7.71	5.02	8.58	7.48

By the term "consisting essentially of" is meant that additional ingredients may be added provided they do not substantially alter the nature of the composition. Substances which cause the biodissolution to drop below 150 ng/cm<sup>2</sup>/hr or which lower the  $\Delta T$  to a value below 350°F are substances which do substantially alter the composition. Preferably, the glass compositions are free of iron oxides, lead oxides, fluorine, phosphates (P<sub>2</sub>O<sub>5</sub>), zirconia, and other expensive oxides, except as unavoidable impurities. It should be noted that while rotary process glass compositions are in general unsuitable for pot and marble fiberization, the reverse is not true, and the subject invention glass compositions should yield fibers prepared by the rotary process which have yet higher rates of biodissolution.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

**What Is Claimed Is:**

1. Glass fibers exhibiting high chemical resistance, moisture resistance, and biosolubility, said glass fibers prepared from a glass composition suitable for pot and marble fiberization, said composition consisting essentially of, in mol percent:

SiO <sub>2</sub>	66 -- 69.7
Al <sub>2</sub> O <sub>3</sub>	0 -- 2.2
RO	7 -- 18
R <sub>2</sub> O	9 -- 20
B <sub>2</sub> O <sub>3</sub>	0 -- 7.1

said glass composition having a C(acid)  $\geq 1.95$ , a C(bio)  $\leq 2.30$ , a C(moist)  $\geq 2.46$ , a difference,  $\Delta T$ , between HTV ( $10^3$  poise) and liquidus in excess of 350°F, and a biodissolution in excess of 150 ng/cm<sup>2</sup>/hr when fiberized by pot and marble fiberization.

2. The glass fibers of claim 1 wherein said composition consists essentially of, in mol percent:

SiO <sub>2</sub>	66 -- 69.0
Al <sub>2</sub> O <sub>3</sub>	0 -- 2.2
RO	7 -- 16
R <sub>2</sub> O	9 -- 19
B <sub>2</sub> O <sub>3</sub>	0 -- 7.1

3. The glass fibers of claim 1 wherein said composition consists essentially of, in mol percent:

SiO <sub>2</sub>	66 -- 68.25
Al <sub>2</sub> O <sub>3</sub>	0 -- 2.2
RO	7 -- 13
R <sub>2</sub> O	11 -- 18
B <sub>2</sub> O <sub>3</sub>	0 -- 7.1

4. The glass fibers of claim 1 wherein  $\Delta T$  is at least about 425°F.

5. The glass fibers of claim 2 wherein  $\Delta T$  is at least about 425°F.

6. The glass fibers of claim 3 wherein  $\Delta T$  is at least about 425°F.

7. The glass fibers of claim 1 wherein said fibers have a measured biodissolution rate when fiberized by pot and marble fiberization of greater than 300 ng/cm<sup>2</sup>/hr.

8. The glass fibers of claim 2 wherein said fibers have a measured biodissolution rate when fiberized by pot and marble fiberization of greater than 300 ng/cm<sup>2</sup>/hr.

9. The glass fibers of claim 3 wherein said fibers have a measured biodissolution rate when fiberized by pot and marble fiberization of greater than 300 ng/cm<sup>2</sup>/hr.

10. The glass fibers of claim 4 wherein said fibers have a measured biodissolution rate when fiberized by pot and marble fiberization of greater than 300 ng/cm<sup>2</sup>/hr.

11. The glass fibers of claim 5 wherein said fibers have a measured biodissolution rate when fiberized by pot and marble fiberization of greater than 300 ng/cm<sup>2</sup>/hr.

12. The glass fibers of claim 6 wherein said fibers have a measured biodissolution rate when fiberized by pot and marble fiberization of greater than 300 ng/cm<sup>2</sup>/hr.

13. The glass fibers of claim 1 wherein  $\Delta T$  is at least about 425°F and the measured biodissolution of



fibers prepared by pot and marble fiberization is greater than about 400 ng/cm<sup>2</sup>/hr.

14. The glass fibers of claim 2 wherein  $\Delta T$  is at least about 425°F and the measured biodissolution of fibers prepared by pot and marble fiberization is greater than about 400 ng/cm<sup>2</sup>/hr.

15. The glass fibers of claim 3 wherein  $\Delta T$  is at least about 425°F and the measured biodissolution of fibers prepared by pot and marble fiberization is greater than about 400 ng/cm<sup>2</sup>/hr.

16. The glass fibers of claim 1 wherein  $C(\text{acid}) \geq 2.00$ ,  $C(\text{bio}) \leq 2.23$  and  $C(\text{moist}) \geq 2.50$ .

17. The glass fibers of claim 1 wherein  $C(\text{acid}) \geq 2.00$ ,  $C(\text{bio}) \leq 2.20$  and  $C(\text{moist}) \geq 2.60$ .

18. Flame attenuated pot and marble fiberized glass fibers, said fibers having an outer shell depleted of a position of volatile oxides, said fibers prepared from a glass composition comprising, in mol percent:

SiO <sub>2</sub>	66 -- 69.0
Al <sub>2</sub> O <sub>3</sub>	0 -- 2.2
RO	7 -- 16
R <sub>2</sub> O	9 -- 19
B <sub>2</sub> O <sub>3</sub>	0 -- 7.1

characterized by a  $C(\text{acid}) \geq 2.00$ , a  $C(\text{bio}) \leq 2.23$ , a  $C(\text{moist}) \geq 2.50$ , a difference  $\Delta T$  between the HTV (10<sup>3</sup> poise) and liquidus greater than 300°F, said fibers exhibiting a biodissolution of greater than about 150 ng/cm<sup>2</sup>/hr.

19. The fibers of claim 18, wherein said  $C(\text{acid}) \geq 2.00$ , said  $C(\text{bio}) \leq 2.23$ , said  $C(\text{moist}) \geq$

2.50, said  $\Delta T$  is greater than about 400°F, said fibers exhibiting biodissolution  $\geq 300$  ng/cm<sup>2</sup>/hr.

20. The fibers of claim 18, wherein said glass composition comprises, in mol percent:

SiO <sub>2</sub>	66 -- 68.25
Al <sub>2</sub> O <sub>3</sub>	0 -- 2.2
RO	7 -- 13
R <sub>2</sub> O	11 -- 18
B <sub>2</sub> O <sub>3</sub>	0 -- 7.1

said C(acid)  $\geq 2.00$ , said C(bio)  $\leq 2.20$ , said C(moist)  $\geq 2.60$ , said  $\Delta T$  is greater than about 400°F, said fibers exhibiting biodissolution  $\geq 300$  ng/cm<sup>2</sup>/hr.

21. An acid and moisture resistant glass fiber prepared from a glass composition consisting essentially of, in mol percent:

SiO <sub>2</sub>	66.5 - 67.8
Al <sub>2</sub> O <sub>3</sub>	0.5 - 1.5
B <sub>2</sub> O <sub>3</sub>	5.0 - 7.0
CaO	3.0 - 7.0
MgO	3.0 - 7.0
Na <sub>2</sub> O	14.0 - 17.0
K <sub>2</sub> O	0.1 - 0.4

wherein the sum of CaO and MgO is between about 8.0 and 12.0, said glass fiber exhibiting a  $\Delta T$  greater than 400°F and a biodissolution greater or equal to about 350 ng/cm<sup>2</sup>/hr.

# INTERNATIONAL SEARCH REPORT

Inte: 5 Application No

PCT/US 98/05636

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 108 957 A (COHEN ISABELLE ET AL) 28 April 1992 cited in the application see table 3 Glass #6	1-21
A	EP 0 588 251 A (SCHULLER INT INC) 23 March 1994 see page 5, line 24 see page 5, line 30 see page 12, line 15 see table 5 fiber 6	1-21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

15 July 1998

Date of mailing of the international search report

23/07/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Somann, K

# INTERNATIONAL SEARCH REPORT

onal Application No

PCT/US 98/05636

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	POTTER R M ET AL: "GLASS FIBER DISSOLUTION IN A PHYSIOLOGICAL SALINE SOLUTION" GLASTECHNISCHE BERICHTE; vol. 64, no. 1, 1 January 1991, pages 16-28, XP000178832 see table 2 Glasses #6 and 29 ----	1-21
A	US 3 663 192 A (PERRY WALTER MERTON) 16 May 1972 see column 1, line 12 see column 2, line 23 - line 26 see column 5, line 19 - line 62 ----	1-21
A,P	US 5 634 954 A (KERN CHARLES F) 3 June 1997 see column 3, line 65 -----	1-21

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/US 98/05636

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5108957	A	28-04-1992	FR 2650821 A	15-02-1991
			FR 2658182 A	16-08-1991
			AU 630484 B	29-10-1992
			AU 6002590 A	14-02-1991
			CA 2022446 A	12-02-1991
			CN 1049834 A,B	13-03-1991
			CN 1093066 A	05-10-1994
			DE 69007369 D	21-04-1994
			DE 69007369 T	13-10-1994
			DK 412878 T	18-07-1994
			EP 0412878 A	13-02-1991
			ES 2053139 T	16-07-1994
			FI 100795 B	27-02-1998
			HR 950203 A	30-06-1997
			HU 210633 B	28-06-1995
			IE 66323 B	27-12-1995
			JP 3093650 A	18-04-1991
			MX 172027 B	29-11-1993
			NO 178023 B	02-10-1995
			PL 165859 B	28-02-1995
			PL 171355 B	30-04-1997
			PT 94971 A,B	18-04-1991
			SI 9011548 A	31-12-1994
			US 5250488 A	05-10-1993
EP 0588251	A	23-03-1994	US 5401693 A	28-03-1995
			AT 151061 T	15-04-1997
			CA 2106412 A,C	19-03-1994
			DE 69309374 D	07-05-1997
			DE 69309374 T	23-10-1997
			DK 588251 T	29-09-1997
			EP 0739862 A	30-10-1996
			JP 2588360 B	05-03-1997
			JP 6321578 A	22-11-1994
US 3663192	A	16-05-1972	NONE	
US 5634954	A	03-06-1997	NONE	

**THIS PAGE BLANK (USPTO)**